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EXTRACTION OF "ESSENCE" FROM TOBACCO STEMS

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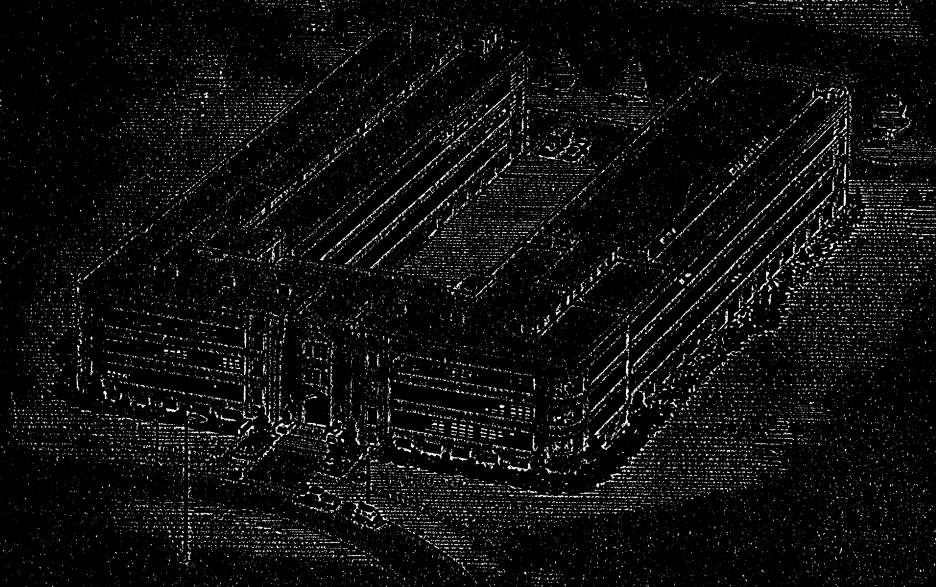

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EXTRACTION OF "ESSENCE" FROM TOBACCO STEMS

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This Laboratory undertook the study of "essence" recovery because it was felt that it might be used to improve the lower grade tobaccos or to impart a tobacco aroma to paper, wood, or similar materials used in packing tobacco products. This "essence," a fragrant fraction having a characteristic tobacco aroma, would be recovered from stems or low-grade materials, which at present are used only for recovery of nicotine.

Since odor and taste are interdependent, many investigators have studied the essential oils of tobacco flowers (1, 2, 3, 4) and leaves (5, 6, 7, 8, 9, 10, 11) and of the resins in tobacco (12, 13, 14, 15, 16, 17, 18, 19) which contribute to the over-all tobacco aroma. Many patents have been issued which describe methods of recovering the flavor of tobacco; these include water or organic solvent extraction (20, 21, 22, 23, 24, 25, 26, 27) and steam extraction (28). Inferior grades of tobacco have been improved by selective fermentation with microorganisms (29, 30, 31) by addition of inorganic substances such as hydrochloric acid (32, 33), and by addition of sweetening agents and synthetic tobacco flavors (34, 35, 36, 37).

Benzene, ether, petroleum ether, and alcohol have been commonly used for extraction of resin fractions from tobacco. The literature cited on the study of essential oils of tobacco indicates that the best method of obtaining an essence would be to steam distill the tobacco or extract it with water, distill the extract so obtained, and concentrate or extract the distillate. Aqueous methods were therefore studied first. This study also compared the efficiency of other organic solvents, not mentioned in the literature, for recovery of tobacco essence. The purpose was to find the best method of obtaining an essence characteristic of the variety of tobacco being studied.

Methods of "Essence" Recovery

Aqueous Methods: Two general methods were employed: water leaching, with subsequent distillation of the extract, and steam stripping.

In the first, 300 grams of Havana Seed Leaf stems, ground on a Wiley mill to pass a 20-mesh screen, was mixed with 1 liter of water. The mixture was stirred for 1 hour at room temperature. The water extract was decanted off, and distilled through an 80-plate Modified Stedman fractionating column. Samples of distillate were taken in 3-cc. fractions until 30-cc. had been collected. These fractions were evaluated for quality and strength.

The aqueous extract obtained had a pH of 6.7. Modifications of the procedure were to adjust the extract to pH 3.0 with sulfuric acid or to pH 8.5 with sodium hydroxide before distillation. Also the ground tobacco stems and water were mixed together in the distillation flask, and distillation was carried on directly.

In steam stripping, 80 grams of the ground stems was put in a glass U-tube and maintained at a temperature of 130° C. by immersion of the U-tube in an oil bath. Steam was passed through the charge at a rate of 32 grams per hour and upon leaving the tube condensed until 80-cc. of distillate was collected. Fractions similar to those obtained in the leaching and distillation method were recovered. One modification of this procedure was to collect the distillate and extract it with ether. The ether was then removed by evaporation, leaving an aromatic residue.

The fractions collected by these aqueous methods were compared with a control consisting of the original ground stems. The fraction obtained by stem-stripping received the highest rating.

The panel used in evaluating the fractions agreed that none were very nearly like the control in quality. There was no difference in the quality of the fractions obtained by direct steam distillation and by distillation of the aqueous extract at the original pH. Although the ether extracted fraction from the steam distillation procedure had a pleasant aromatic odor, it did not compare in quality with the original stems. However, most of the early fractions from each procedure possessed a much stronger odor than the control. In all these procedures, the residual tobacco stems possessed a tobacco aroma.

Solvent Methods: The inferior results obtained from the aqueous methods indicated that an organic solvent method should be developed. To determine the best solvent to use, 100-gram samples of the ground stems were extracted for 10 hours in a Soxhlet extractor. Solvents used were chloroform, benzene, ethanol (95 percent), methanol, acetone, t-butanol, and iso-propanol. Residues obtained after removal of solvents by evaporation weighed 2.9, 2.1, 8.6, 8.7, 3.0, 3.1, and 4.4 grams, respectively. The residues were dissolved in alcohol and impregnated into filter paper for quality evaluation. Ethanol extraction produced the most representative essence concentrate; t-butanol, methanol, acetone, chloroform, benzene and iso-propanol extractives were next in order of preference. The residual tobacco stems had no odor when dry.

The best aqueous essence was compared with the solvent-prepared extracts. The solvent extractives were superior except in the case of benzene and iso-propanol.

In all extractions with ethanol, potassium nitrate crystals precipitated upon cooling.

Extraction Procedures

Soxhlet Extraction: The time required to completely extract the alcohol-solubles was studied. Ten Soxhlet extractors were each charged with 100 grams of Havana Seed Leaf stems. The extraction was started simultaneously in all the units, 95 percent ethanol being used as the solvent. One extractor was stopped at each 2-hour interval. The alcohol was evaporated on the

steam bath, and the residue weighed. The residue was then treated with 75-cc. of 95 percent alcohol and filtered to remove the potassium nitrate salt. The salt was washed with alcohol, dried, and weighed. The alcohol was evaporated off the filtrate, and the alcohol-solubles were determined by weighing the residue. The residue was then extracted with 50-cc. of benzene. The benzene was removed from this extract, and the residue weighed to determine the benzene-solubles. The results are summarized in Table 1.

Table 1. Time required for complete extraction of alcohol solubles

Time of extraction Hours	Residue from extract Grams	Salts removed Grams	Alcohol solubles Grams	Benzene solubles Grams
2	7.0	2.6	4.4	0.5
4	7.6	2.8	4.8	.7
6	8.2	3.2	5.0	.6
8	10.2	4.8	5.4	.7
10	11.4	5.0	6.4	.9
12	10.4	3.9	6.5	1.0
14	13.6	6.8	6.8	1.1
16	12.7	5.8	6.9	.9
18	14.2	7.3	6.9	1.1
20	12.0	5.2	6.8	1.0

It can be seen from the table that the time required for complete extraction is approximately 12 hours. If longer time is used, more salts are removed, but there is no substantial increase in the amount of alcohol solubles or benzene solubles recovered.

The quality of the total alcohol-soluble extract was compared with that of the benzene-soluble extract. The alcohol-soluble extract was preferred.

Batchwise Extraction: The proper temperature and time required for batchwise extraction were investigated. One hundred-gram samples of ground Imported Cuban stems were placed in 1-liter beakers and covered with 400-cc. of 95 percent alcohol. The mixtures were heated to 40°, 60°, or 78°C. for 0, 1, 2, or 3 hours. They were then poured into a filter and washed with 150-cc. of 95 percent alcohol. The filtrates were examined for alcohol-soluble and benzene-solubles as outlined above in the Soxhlet procedure. The results are summarized in Table 2.

Table 2. Effects of time and temperature in batchwise extraction

Time Hours	Alcohol solubles			Benzene solubles		
	40° Grams	60° Grams	78° Grams	40° Grams	60° Grams	78° Grams
0	3.4	4.5	4.6	1.2	1.4	1.7
1	4.4	5.7	7.7	1.5	1.9	2.2
2	5.5	6.5	7.5	1.7	2.1	2.5
3	6.5	6.1	7.5	2.1	2.3	2.6

For comparative purposes, a 100-gram sample of stems was extracted in a Soxhlet for 12 hours. Another sample was extracted batchwise at room temperature for 24 hours. The Soxhlet procedure gave 9.4 grams of alcohol-solubles and 2.5 grams of benzene-solubles, whereas that done batchwise gave 4.0 and 1.3 grams, respectively.

As can be interpreted from Table 2, batchwise extraction for 2 hours at 78° C. was comparable with the Soxhlet procedure, but the extraction at room temperature was only about 50 percent as efficient even after 24 hours.

Large-Scale Extraction: A large-scale batchwise extraction of Pennsylvania Filler stems and White Burley stems was carried out. A 200-gallon steam-jacketed stainless steel kettle was charged with 400 pounds of stems ground in a hammer mill having a 1/2-inch mesh screen. The stems were covered with 125 gallons of 95 percent alcohol and then heated to 78° C. within 1 hour. The mass was kept at this temperature for 2 hours. The alcohol was then drained off while still hot. Eighty gallons of fresh alcohol was added to the stems, and the mass was heated to 78° C. The alcohol was immediately drained off and added to the first extract. The extracts from several batches were accumulated and concentrated to approximately one-tenth the original volume by distilling off the alcohol in a 100-gallon stainless steel still. The recovered alcohol was used again in subsequent extractions.

The concentrated extract was filtered through a plate-and-frame-filter press to remove the precipitated salts. The resulting extract was comparable with that obtained in the laboratory. Two-hundred and sixty pounds of essence from 883 pounds of Pennsylvania Filler stems and 298 pounds from 1221 pounds of White Burley stems were produced in this manner. The Pennsylvania Filler and White Burley extracts contained 1.59 and 2.33 percent of nicotine, respectively, an average recovery of about 70 percent of the nicotine in the original stems.

To determine whether any desirable fraction was lost during the evaporation steps in the solvent methods, the alcohol extract obtained from a Soxhlet extraction was distilled through an 80-plate column until the temperature in the still pot reached 120° C. No odor-bearing fraction was obtained before the alcohol fraction had been completely distilled. The water fraction, which was collected next, had the same odor as the distillate from the aqueous distillation method at pH 6.7. Organoleptic tests showed that it made little difference in the quality of the essence whether this water fraction was returned to the still residue or discarded.

Samples of stems as brought into the laboratory contained from 22 to 30 percent moisture. This necessitated drying to prevent fermentation. They were air-dried until the moisture content was 12.5 to 15 percent. Throughout the drying period (3-7 days), a strong tobacco odor filled the room in which the drying was being done. To ascertain whether any loss in the quality of the essence resulted from this drying method, samples of the stems were extracted both before and after drying. Although the extracts made from the dried stems actually were slightly preferred to those made from the wet stems, the tests showed no significant difference.

ORGANOLEPTIC TESTS

Twenty-nine employees of the laboratory, smokers and nonsmokers of both sexes, were selected at random for a testing panel. The tests were made in a room in which smoking was prohibited. No discussion of ratings given by members of the panel was permitted prior to the time any individual made his ratings. In the preliminary tests, when the method of extraction was being investigated, controls consisting of the original tobacco stems were used. In these tests, a blank was also presented to the testing panel without any indication that it was included. Since no suitable control could be used when the varieties were being compared, it was necessary to rely on the individual's judgment and previous training for quality evaluation. In two instances, the panel was presented with identical samples at least 1 day apart, whereupon the same order of ratings resulted.

S and S filter paper No. 597, cut into 4 by 5 inch sheets weighing approximately 1.2 grams each was impregnated with the extract from its alcoholic solution. The paper was allowed to dry in air at room temperature until no odor of alcohol could be detected (about 1 hour). The sheets of impregnated paper were then placed in amber-colored glass bottles 5-1/2 inches tall and 3 inches in diameter with a 1-3/4-inch opening. The bottles and screw caps, from which the plastic and paper inserts had been removed, were previously cleaned with soap and water, rinsed with water and alcohol, and then dried thoroughly. No foreign odor could be detected in the bottles. The bottles, labeled only with a code number, were then given to the panel, which rated the samples from best to worst and from strongest to weakest. No numerical values were assigned.

To determine the correlation between quality and strength ratings and to find the concentration of extract required for best testing, the filter paper sheets were impregnated with concentrations of extract equivalent to that obtained from 8, 4, 2, 0.5, 0.25 and 0.125 grams of tobacco. The panel rated the samples for strength in their exact order of concentration. However, the quality rating was in the following order: 4, 2, 8, 0.5, 0.25 and 0.125. The last two concentrations were described as "perfume like." In all the other comparative tests, a concentration of extract equivalent to that obtained from 4 grams of tobacco was used to impregnate the filter paper sheets. The blank mentioned previously was just an untreated sheet of the paper.

Numerical values were given to the rank, 1 for the weakest or lowest quality, 2 for the next strongest or better quality and so on in order until the best quality and strongest sample had the highest number. These numerical values were added to obtain the final result. Quality and strength ratings of the samples, scored independently, showed no correlation with each other.

No more than 6 samples were presented to the panel at any one time. The best samples from one test were then compared with the best of another test until the final over-all order of the varieties was obtained.

Extraction of Varieties of Stems

The tobacco samples were air dried and ground in the Wiley mill through a 1/4-inch screen. The moisture content was determined by drying 50 grams of the sample in a Freas oven for 24 hours at 110° C. Ten extra large (500-ml. capacity to the siphon arm) Soxhlet extractors, equipped with 1-liter flasks, were each charged with 100 grams of stems, and 750 cc. of 95 percent ethanol was put in each flask. Extraction was carried on for 10 to 12 hours. The extracts were combined, and the alcohol was removed by distillation until a volume of 800 cc. remained in the still pot. The extract was cooled to room temperature and filtered. The salt retained on the filter was washed with 100 cc. of 95 percent alcohol. The filtrates were combined, the alcohol was removed by evaporation on the steam bath, and the residue was weighed. The residue was dissolved in 200 cc. of 95 percent alcohol, the alcohol solution was filtered, and the final volume of the extract was adjusted to 250 cc. Any salt removed in this last filtration was combined with that obtained in filtering the concentrated extract from the Soxhlet extractors. The salt fraction was dried and weighed.

Ten varieties of stems from cigar type tobaccos and three varieties from cigarette types were extracted, and a panel evaluated the extracts for desirable aroma. The varieties were rated in the following decreasing order: Connecticut Broad Leaf, Connecticut Shade, Red Burley, Imported Cuban, Imported Cuban Wrapper, Pennsylvania Filler, Flue Cured, Havana Seed Leaf, Light Burley, Wisconsin, Sumatra, Ohio Broad Leaf and One Sucker. In developing the proper procedure for extraction, the leaves and stems of Havana Seed Leaf tobacco were extracted similarly. In every instance in which comparable methods were employed for leaves and stems, the leaves gave a better quality and stronger extract than did the stems. The difference, however, was not so great as expected.

The method used to extract the essence from the stems also removed from 84 to 93 percent of the nicotine contained in the stems. Data on removal of nicotine are included in Table 3.

If the extract is to be used for enhancing smoking tobacco, the additional nicotine may be objectionable unless only a small percentage of the extract is required. The nicotine was removed quantitatively from the essence extract by a modification of the alcohol procedure. After the alcohol was removed from the extract, the residue was shaken between dilute hydrochloric acid and benzene. The benzene extract was removed and washed with distilled water. The benzene was removed by evaporation, and the residue was redissolved in alcohol for use. In a typical experiment on Imported Cuban stems, 84.6 grams of alcohol solubles was obtained from 1 kg. of stems, whereas 19.4 grams of benzene solubles were obtained by the nicotine-removal technique. In the preliminary experiments it was proved that an extract containing all the alcohol solubles was preferred to one containing only the benzene solubles, therefore the nicotine removal technique should be used only when necessary.

Table 3 shows the quantity of inorganic salts and alcohol solubles obtained from each variety.

Table 3. Nicotine, inorganic salts and alcohol solubles recovered from tobacco stems by the alcohol method

Variety	Moisture	Nicotine in stems	Nicotine removed	Inorganic salts removed from 1 kg. stems	Alcohol-solubles removed from 1 kg. stems	Nicotine in essence[b]
	Percent	Percent[a]	Percent	Grams	Grams	Percent
Connecticut Broad Leaf	13.0	0.91	83.5	45.1	69.6	2.99
Connecticut Shade	12.6	.66	89.6	44.8	102.5	2.37
Red Burley	5.6	1.12	91.0	31.8	70.5	3.86
Imported Cuban	12.8	1.21	87.6	29.3	84.6	4.22
Imported Cuban Wrapper	10.6	.56	96.0	67.2	55.0	1.92
Pennsylvania Filler	15.6	1.03	87.5	57.1	76.9	3.53
Flue Cured	7.6	.46	78.9	46.5	155.5	.67[c]
Havana Seed Leaf	12.6	1.68	86.5	57.6	69.9	5.91
Light Burley	6.5	.58	87.9	37.4	73.0	1.95
Wisconsin	15.2	1.27	89.0	49.0	90.8	4.44
Sumatra	14.8	.84	93.1	59.1	61.5	3.08
Ohio Broad Leaf	15.0	1.44	90.4	43.2	87.7	5.13
One Sucker	13.4	1.94	92.3	40.5	93.6	7.14

a *Moisture-free basis.*

b *Final volume of extract was 250 cc. This contained the fragrant fraction from 1 kg. of stems.*

c *Final volume of this extract was 500 cc.*

The quantity of salt removed from the Flue Cured stems represents the insoluble fraction in the 800-cc. volume of alcohol extract to which the extracts were concentrated before filtration. Since this salt fraction was not of a definite crystalline nature, it was gummy and difficult to handle. It probably did not represent even closely the amount of potassium nitrate in the original sample, but was contaminated with sugars and tars. In all the other varieties, the salt fraction was crystalline and almost pure potassium nitrate.

Recommended Procedure for Preparation of Tobacco "Essence"

Laboratory: The stems are air-dried to 12-14 percent moisture and ground in a Wiley mill to pass through a 1/4-inch screen. An extra large (500-ml. capacity to the siphon arm) Soxhlet extractor fitted with a 1-liter flask is charged with 100 grams of the stems; 750-cc. of 95 percent alcohol is

placed in the flask. Extraction is carried on for 12 hours. The alcohol is then drained off and concentrated to approximately 75 cc., cooled and filtered to remove the inorganic salts. The filtrate may be used directly or further concentrated to approximately 25 cc.

Large-scale: The stems are air-dried to 12-14 percent moisture and ground in a hammer mill to pass through a 1/2-inch screen. A 200-gallon stainless steel steam-jacketed kettle equipped with a reflux condenser and false bottom is charged with 400 pounds of stems. Approximately 125 gallons of 95 percent alcohol is added (sufficient to cover the stems). The mass is heated to 78° C. and maintained at that temperature for 2 hours. The hot alcoholic extract is drained off through a port in the bottom of the kettle. The port is closed, and 80 gallons of fresh 95 percent alcohol is added to the kettle. The mass is heated to 78° C., and the hot alcoholic extract is immediately drained off through the port and combined with the first extract. Approximately 160 gallons of solution is obtained. This is concentrated in a stainless steel still to about 16 gallons, cooled, and filtered to remove the inorganic salts. The concentrate may be used as is or further concentrated to 4-5 gallons.

SUMMARY

Aqueous and solvent methods were compared for the preparation of a tobacco essence of characteristic aroma. Essences were prepared from 10 varieties of cigar type and 3 varieties of cigarette type tobacco stems. By the use of organoleptic tests, an order of preference was established. A simple method of essence extraction using 95 percent ethanol is presented. The quantities of salts, alcohol solubles, and nicotine removed from the stems of these varieties were determined.

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